



A thermogravimetric study of the partial oxidation of methanol for hydrogen production over a Cu/ZnO/Al₂O₃ catalyst

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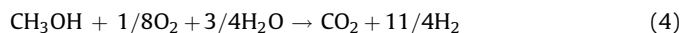
ABSTRACT

The partial oxidation of methanol for the production of hydrogen was investigated in both a fixed-bed microreactor and in a thermogravimetric analyzer (TG-FTIR) from 180 °C to 250 °C using a commercial Cu/ZnO/Al₂O₃ catalyst. In the microreactor, a hot spot in the undiluted catalyst bed of 4 K and 32 K was observed at 180 °C and 220 °C, respectively. Methanol conversion was strongly accelerated between 180 °C and 220 °C. In the TG-FTIR experiments, the reduced copper was completely oxidized to cuprite, Cu₂O, with increasing time-on-stream in the presence of oxygen and methanol (O₂/MeOH = 0.5) at 180 °C. The selectivity to formaldehyde increased in the same manner as the catalyst was oxidized to cuprite. In contrast, at 250 °C the catalyst remained completely reduced for the same O₂/MeOH ratio. Two main reaction pathways are proposed explaining the influence of the copper oxidation state on the product distribution.

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1. Introduction

Methanol can be used as a fuel for direct methanol fuel cells (DMFC) which are regarded as an interesting option for powering small to midsize electronic devices. However, the efficiency of the DMFC is lower compared to hydrogen driven fuel cells. An efficient reforming of methanol to produce hydrogen can increase the overall efficiency of methanol fuel cell systems [1]. Furthermore, reformed methanol fuel cells may be used in fuel cell driven vehicles since they can help to reduce greenhouse gas emissions [2]. Hydrogen can be extracted on-board from methanol by steam reforming (SR, Eq. (1)), partial oxidation (POX, Eq. (2)), or a combination of both reactions (autothermal reforming ATR, Eq. (4)). Heterogeneous copper-based catalysts exhibit an excellent selectivity to hydrogen since they do not catalyze the methanation reaction, as opposed to nickel and other metals.



A compact fuel processor equipped with a commercially available Cu/ZnO catalyst was presented in the literature [3]. Several studies have been undertaken to investigate the properties of copper-based catalysts for the steam reforming reaction [4–12].

The dry partial oxidation reaction (POX, Eq. (2)) has received less attention [13]. The stability of copper-based catalysts is limited by sintering of the copper crystallites above ca. 300 °C. Furthermore, fully oxidized copper has no activity for POX, and only total oxidation (TOX, Eq. (3)) to carbon dioxide and water is observed [14].

The influence of oxygen on the reaction mechanism of the dry partial oxidation is still an open question. It has been shown that activity and selectivity of the Cu/ZnO catalysts strongly depend on the oxygen concentration of the feed. It was suggested that copper metal (Cu⁰) is active for the partial oxidation of methanol to produce hydrogen whereas Cu^I favors the formation of water and carbon monoxide [14]. A detailed study of the copper oxidation state over Cu/ZnO/Al-catalysts using X-ray photoelectron spectroscopy revealed that at a low oxygen concentration in the feed (O₂/MeOH = 0–0.25) Cu⁰ is the dominating species, independent of the temperature. A temperature dependence of the oxidation state was observed if a higher oxygen content (O₂/MeOH = 0.42) was applied: the formation of Cu^I was detected between 470 K and

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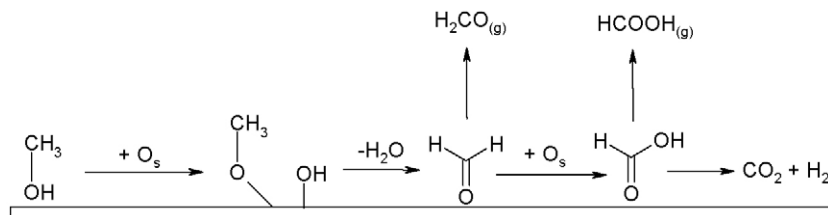


Fig. 1. Surface reaction network of the dry partial oxidation of methanol over a copper catalyst.

510 K, above 530 K only Cu^0 was detected [15]. The oxidation state of the catalyst during the methanol POX may be also affected by the support material [15,16]. The methanol POX over an unsupported copper catalyst was also investigated by in-situ X-ray absorption spectroscopy [17–20]. It was found that the activity of the catalyst was a function of the O_2/MeOH ratio in the feed. It was proposed that the active structure of the catalyst consisted of a Cu^0 -lattice in which oxygen atoms are intercalated.

The oxidative steam reforming of methanol over a Cu/ZnO catalyst was also investigated by means of in-situ time-resolved X-ray absorption spectroscopy [21].

The results of this study with respect to the oxidation state of the catalyst were similar to the dry POX: the catalyst was oxidized at low temperature and reduced at higher temperature.

The formation of intermediate products (i.e. methyl formate and formaldehyde) during the partial oxidation of methanol for hydrogen production under various reaction conditions has been reported in the literature. The decomposition of methanol over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts yields hydrogen and CO . Methyl formate, HCOOCH_3 , is formed as an intermediate [22]. However, to our knowledge a detailed study of the conditions at which these intermediates are formed has not been published.

The mechanism of the dry partial oxidation (POX, Eq. (2)) on $\text{Cu}(110)$ surfaces was also studied [23–26]. Formaldehyde and formate species are involved in the surface reaction network (Fig. 1).

It was found that for oxygen-rich mixtures formaldehyde is the major product but when methanol was in 5:1 excess, formate (HCOOH) was produced [24]. A combustion-reforming mechanism was proposed for Cu/ZnO catalysts prepared by a microemulsion technique in the low temperature regime [27]. Here, methanol is totally oxidized to water and carbon dioxide. In a subsequent step, steam reforming of methanol occurs.

The aim of this study was to gain a better understanding of the reactions involving both methanol and oxygen on a commercially available $\text{Cu}/\text{ZnO}/\text{alumina}$ catalyst with a focus on the catalyst oxidation state at different reaction conditions. Furthermore, the conditions where intermediate products like methyl formate and formaldehyde are formed were investigated. Thermogravimetric analysis coupled with FTIR spectroscopy is an excellent tool to study the bulk oxidation state of a catalyst in-situ, because, in the absence of coking, this is directly related to the weight change of the catalyst.

2. Experimental

A commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst obtained from Johnson Matthey was used for all experiments. The catalyst consisted of 35 wt% Cu , 37 wt% Zn and 5.4 wt% Al (ICP analysis). The active copper surface area of the catalyst was determined by N_2O decomposition experiments to be $16 \text{ m}^2/\text{g}$. This corresponds to a dispersion of 7.1% assuming that the number of surface atoms of copper is $1.47 \times 10^{19} \text{ atoms}/\text{m}^2$ [28].

2.1. Microreactor experiments

Microreactor experiments were performed in a fixed-bed tubular reactor (6.35 mm O.D., 4 mm I.D.) made of glass-lined stainless steel, and fitted with a thermowell (1.5 mm O.D.) for measuring axial temperature profiles. The $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst was crushed and sieved to a particle size range of 125–250 μm , 750 mg of which were sandwiched in the reactor between two layers of SiC . The reactor was placed in the isothermal zone of an electrically heated oven developed at our institute. Reduction of the catalyst was performed by flowing a mixture of 20% $\text{H}_2/80\% \text{ N}_2$ at 300 °C for 2 h. Liquid methanol was fed to the reactor at a weight hourly space velocity (WHSV) of 2.2 h^{-1} . Before entering the reactor, the methanol was vaporized in a heated coil and diluted with nitrogen. The feed gas composition was $\text{MeOH}:\text{O}_2:\text{N}_2 = 5.5:1:120$. The gaseous effluent was analyzed for CO , CO_2 , H_2 , N_2 , O_2 , CH_4 and methyl formate (MF) using a gas chromatograph (Agilent 6890 plus) equipped with a two-column switching system and a thermal conductivity detector. The conversion of methanol (X_{MeOH}) and the yields (Y) of CO , CO_2 , H_2 and methyl formate (MF, HCOOCH_3) were calculated from the molar flows:

$$X_{\text{MeOH}} = \frac{(\text{MeOH}^{\text{in}} - \text{MeOH}^{\text{out}})}{\text{MeOH}^{\text{in}}}, \quad Y_{\text{CO}} = \frac{\text{CO}}{\text{MeOH}^{\text{in}}},$$

$$Y_{\text{CO}_2} = \frac{\text{CO}_2}{\text{MeOH}^{\text{in}}}, \quad Y_{\text{H}_2} = \frac{\text{H}_2}{2\text{MeOH}^{\text{in}}}, \quad Y_{\text{MF}} = \frac{2\text{HCOOCH}_3}{\text{MeOH}^{\text{in}}}$$

2.2. Thermogravimetric experiments

The thermogravimetric experiments were conducted at atmospheric pressure on a Netzsch STA 449 thermogravimetric analyzer coupled to an FT infrared spectrometer (Bruker Tensor 27) for simultaneous gas analysis (MeOH , CO , CO_2 , H_2O , H_2CO , HCOOCH_3). Helium was used as carrier gas in order to minimize buoyancy effects. A mass spectrometer was not available for the experiments.

The samples (100 mg) were placed in an aluminium oxide crucible (volume = 0.8 ml). The size of the catalyst particles used was 125–250 μm . Prior to each experiment, the catalyst was oxidized (12.5% O_2 in He , 80 ml/min, ca. 100 min) at the temperature applied in the experiment and subsequently reduced with hydrogen (20% H_2 in He , 100 ml/min, 20 min). Pure helium, helium saturated with methanol vapor, and oxygen were fed to the TG-FTIR according to the sequences described in Table 1.

Sequences B and C were introduced in order to probe if the adsorption of methanol was reversible. During the experiments, it turned out that the results after the turn off-and-on of methanol (sequence B and C) did not deviate significantly from those obtained after sequence A. Steps B and C were therefore left out in some experiments.

Product gases were analyzed in the FTIR spectrometer for CO , CO_2 , H_2O , methanol, and methyl formate. The methanol conversion

Table 1
TGA reaction sequences

Sequence	He (mmol/min)	MeOH (mmol/min)	O ₂ (mmol/min)	O ₂ /MeOH	WHSV (1/h) ^a
A	2.78	0.45	–	–	8.6
B	2.78	–	–	–	–
C	2.78	0.45	–	–	8.6
D	2.78	0.45	0.045	0.1	8.6
E	2.78	0.45	0.09	0.2	8.6
F	2.78	0.45	0.225	0.5	8.6

^a WHSV: $g_{\text{MeOH}}/(g_{\text{catalyst}} \times h)$. Complete contacting of gas and catalyst is assumed.

was obtained by the integration of the methanol absorption band between 2800 cm^{-1} and 3100 cm^{-1} using the following equation:

$$X_{\text{MeOH}}(t) = \frac{A(t=0) - A(t)}{A(t=0)}$$

with $A(t=0)$: absorbance at $t=0$ (no reaction), $A(t)$: absorbance at the time t .

A methanol gas phase reference spectrum was recorded at room temperature without a catalyst. Difference spectra of the product gas were obtained by subtraction of the reference spectrum from the spectra of the product gas in order to remove the contributions of methanol.

3. Results and discussion

3.1. Fixed-bed microreactor

In an attempt to determine kinetic parameters for the partial oxidation of methanol, two experiments at $180\text{ }^{\circ}\text{C}$ and $220\text{ }^{\circ}\text{C}$ were performed in the fixed-bed microreactor. It has been demonstrated that the hydrogen yields achieved by the dry partial oxidation of methanol decrease if the oxygen content in the feed is increased to the stoichiometric O₂/MeOH ratio of 0.5 [29,30]. Therefore, an O₂/MeOH ratio of 0.18 was applied for the microreactor experiments.

The departure from the oven temperature set point is shown in Fig. 2. At $180\text{ }^{\circ}\text{C}$ the temperature profile was almost flat with a hot spot of 4 K. Products detected in the effluent gas were CO₂, methyl formate, and oxygen (Table 2). No hydrogen was detected at this temperature. A considerable amount of methyl formate was generated. Two reaction pathways are possible: a catalytic dehydrogenation of methanol with a subsequent oxidation of the produced hydrogen or a formation of methyl formate by a

Table 2
Methanol POX over a Cu/ZnO/Al₂O₃ catalyst in a fixed-bed microreactor

T (°C)	X _{MeOH} %	Y _{CO₂} %	Y _{CO} %	Y _{H₂} %	Y _{MF} %	X _{O₂} %
180	16.5	3.2	0	0	4.1	22.4
220	60.8	39.3	8.8	57.2	5.1	100

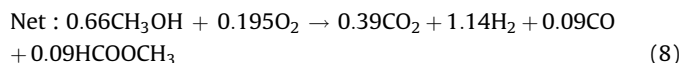
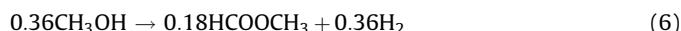
Feed: MeOH:O₂:N₂ = 5.5:1:120. WHSV = 2.2 h^{-1} .

reaction between formic acid and methanol. It has been shown that a variety of copper catalysts are active for the dehydrogenation of methanol to methyl formate at temperatures between $180\text{ }^{\circ}\text{C}$ and $240\text{ }^{\circ}\text{C}$ [7]. It seems, therefore, plausible that the observed yield of methyl formate is generated by a catalytic dehydrogenation pathway. However, a production of methyl formate involving formic acid cannot be ruled out.

At $220\text{ }^{\circ}\text{C}$ the picture changed dramatically. A hot spot of 32 K was observed right at the beginning of the catalyst bed. Thermal conduction in the stainless steel thermowell and probably also thermal dispersion in the gas as well as in the catalyst bed may have smeared the axial temperature profile a bit. In this experiment, H₂, CO₂, CO, and methyl formate were detected in the effluent gas, but no oxygen. The methanol conversion increased to 61%. Due to the low Al content of the catalyst only trace amounts of dimethyl ether were formed.

Obviously, methanol conversion is strongly accelerated between $180\text{ }^{\circ}\text{C}$ and $220\text{ }^{\circ}\text{C}$. This is consistent with the results published by Agrell et al. who investigated the partial oxidation of methanol over a Cu/ZnO catalyst applying a O₂/MeOH ratio of 0.1 [27]. A fast increase in methanol conversion, and H₂ and CO₂ yields around $215\text{ }^{\circ}\text{C}$ were found. Interestingly, formaldehyde instead of methyl formate was formed as a by-product [27]. The authors also observed a hot spot in the reactor which was proposed to be a result of the partial oxidation reaction (Eq. (5)). In contrast to the experiment conducted at $180\text{ }^{\circ}\text{C}$, a considerable amount of CO was generated, which could be a result of the decomposition of methyl formate (Eq. (7)) which is also present in the effluent stream.

According to the previous discussion, the results obtained in the microreactor at $220\text{ }^{\circ}\text{C}$ can be approximated by the following equations:



For the production of CO-free hydrogen it is important to avoid the formation/decomposition of methyl formate. Thus, the aim of the TGA-FTIR study was to investigate the catalyst oxidation state and its influence on the product distribution.

3.2. TGA-FTIR experiments

3.2.1. Temperature-programmed experiment

A temperature-programmed experiment from $150\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ was carried out in the TGA-FTIR setup in order to identify possible temperatures of interests. The heating rate was 10 K/min . In a second set of experiments, isothermal runs were conducted at selected temperatures. The results of the temperature-programmed experiment are shown in Fig. 3. The methanol conversion (X_{MeOH}) increased with increasing reaction temperature. The corresponding TG signal (Fig. 3a) revealed an increase of the catalyst weight in the range of $150\text{ }^{\circ}\text{C}$ to ca. $195\text{ }^{\circ}\text{C}$. At higher

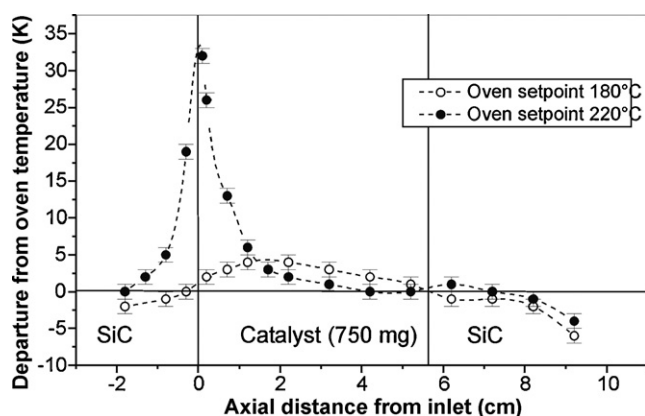


Fig. 2. Axial temperature profiles for the partial oxidation of methanol in a fixed-bed microreactor. Feed: MeOH:O₂:N₂ = 5.5:1:120. WHSV = 2.2 h^{-1} . Oven temperature: ○ $180\text{ }^{\circ}\text{C}$, ● $220\text{ }^{\circ}\text{C}$.

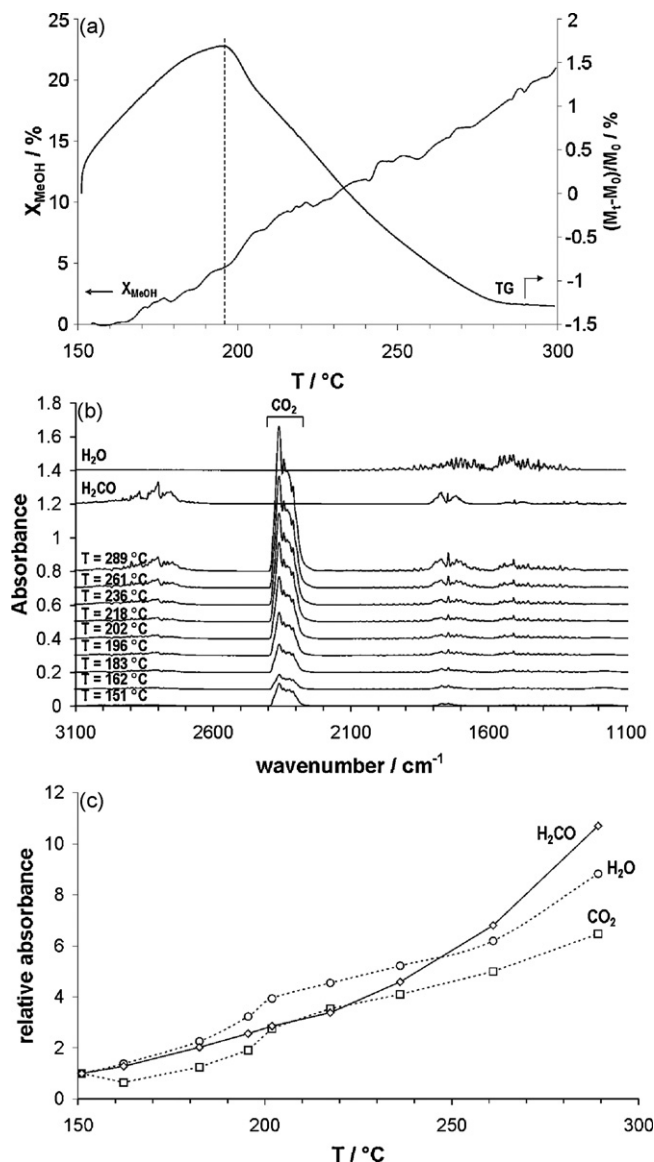


Fig. 3. Methanol POX, conducted in a TGA-FTIR setup. Feed: MeOH:O₂:He = 2:1:12. WHSV = 8.6 h⁻¹ assuming a complete contacting of gas and catalyst. Heating rate: 10 K/min. (a) Relative mass change and methanol conversion, (b) gas phase infrared spectra collected at different temperatures. The methanol background was removed by subtraction. Reference spectra of formaldehyde [31] and water [32] are included, (c) relative absorbance ($A_T/A_{T=150\text{ °C}}$) of water (1653 cm⁻¹), carbon dioxide (2360 cm⁻¹) and formaldehyde (2800 cm⁻¹) as a function of reaction temperature.

temperatures a decrease in weight was measured. The TG curve indicates that the catalyst is oxidized between 150 °C and 195 °C and reduced above 195 °C. The corresponding gas phase infrared spectra of the reaction products are shown in Fig. 3b. The comparison of the spectra with reference spectra revealed that carbon dioxide, water and formaldehyde were formed during the experiments. Carbon monoxide and methyl formate were not detected in the effluent stream. The evolution of the reaction products as a function of the reaction temperature is shown in Fig. 3c. The absorbance of the reaction products at different temperatures were recorded at 1653 cm⁻¹ (water), 1745 cm⁻¹ (formaldehyde, H₂CO) and 2360 cm⁻¹ (carbon dioxide). The data were normalized to the absorbance taken at 150 °C in order to get the relative absorbance. The corresponding evolution profiles (Fig. 3c) revealed an increase in CO₂ and water formation from

150 °C to ca. 200 °C. Above 200 °C, the evolution of CO₂ and water increased less steeply. It should be noted that the shape of the profiles of CO₂ and water are comparable between 150 °C and ca. 260 °C. Above 260 °C, the evolution of carbon dioxide seemed to be less steep compared to the water curve. The evolution of formaldehyde is different from water and carbon dioxide.

The profile showed no distinct feature around 200 °C, as observed in the TG curve and for carbon dioxide and water. The evolution of formaldehyde increased linearly between 150 °C and ca. 220 °C. At higher temperatures, an accelerated production of formaldehyde was observed.

3.2.2. Isothermal experiments

The results of the temperature-programmed experiment indicated that the catalyst was reduced above a temperature around 200 °C and oxidized at lower temperatures. Therefore, isothermal TGA-FTIR runs were carried out at temperatures around 200 °C (180 °C, 200 °C, 220 °C, 250 °C). Different feed compositions were applied (Table 1).

3.2.2.1. Catalyst oxidation. The results of the isothermal experiments are shown in Fig. 4. An increase in weight was observed when the catalyst was exposed to a methanol/helium mixture (Fig. 4, sequences A–C), indicating that methanol is adsorbed on the surface of the catalyst. The amount of adsorbed species remained constant when the methanol vapour was turned off and on again (sequence B and C, respectively) confirming an irreversible adsorption. Assuming that every surface copper atom can adsorb one molecule of methanol one would expect a weight increase of 1.25%. The observed weight increase was 0.4% (180–220 °C) and 0.3% (250 °C). Thus, the effective surface coverage is about 33% (180–220 °C) and 25% at 250 °C.

The introduction of a small amount of oxygen (sequence D; O₂/MeOH = 0.1) did not change the sample weight at any temperature. A small decrease was observed upon a further increase of the oxygen content in the feed (sequence E, O₂/MeOH = 0.2). Whereas the influence of the catalyst temperature in the sequences A–E was small, at an O₂/MeOH ratio of 0.5 (sequence F) the results obtained were strongly dependent on the reaction temperature. At 180 °C, a steady increase of the catalyst mass was observed, levelling off around 4.6% which is close to the expected weight increase assuming an oxidation of copper to cuprite (Cu₂O). An increase in mass was also observed at higher temperatures: at 200 °C the curve levelled off at 2.5%, at 220 °C the final level was ca. 0.8% of the initial mass of the reduced catalyst.

In contrast, a mass loss was recorded at 250 °C. The final mass was close to the initial mass of the reduced catalyst before

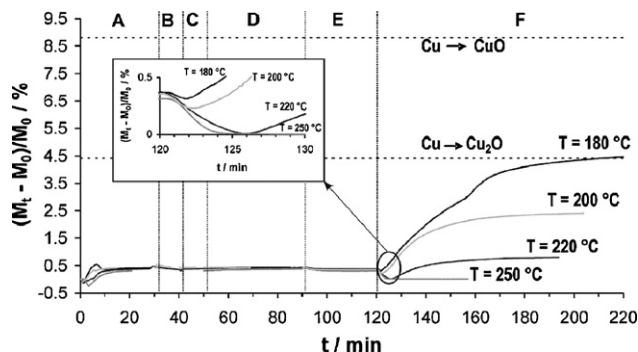


Fig. 4. Isothermal thermogravimetric experiments at different reaction conditions. (A) He/MeOH, (B) He, (C) He/MeOH, (D) O₂/MeOH = 0.1, (E) O₂/MeOH = 0.2 and (F) O₂/MeOH = 0.5. Details of the sequences are presented in Table 1. The catalyst samples were pre-reduced. The broken horizontal lines represent the calculated weight increase for an oxidation of Cu to Cu₂O and CuO, respectively.

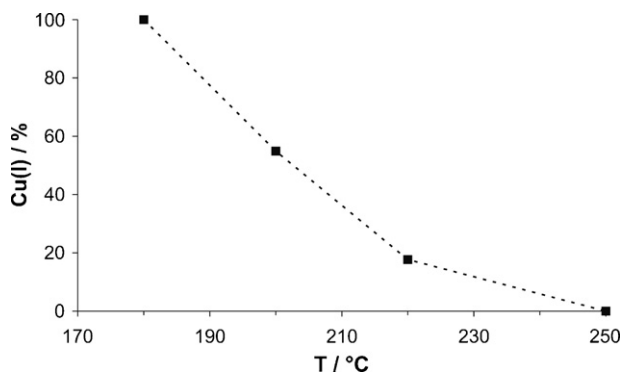


Fig. 5. Bulk oxidation state of the Cu/ZnO/Al₂O₃ catalyst at different temperatures (O₂/MeOH = 0.5).

switching on methanol and O₂. The shape of the TG curves in sequence F is also influenced by the reaction temperature (see insert in Fig. 4). After increasing the oxygen content in the feed from 0.2 to 0.5, an initial weight loss was monitored at 180 °C, 200 °C and 220 °C before the mass increased again. This effect was small at 180 °C and 200 °C and quite large at 220 °C, while it was absent at 250 °C.

It should be noted that no increase in weight was observed at 250 °C (compare Fig. 4, sequence F). An extensive formation of coke on the catalyst can therefore be ruled out. This allows an estimation of the bulk oxidation state of the equilibrated catalyst from the isothermal thermogravimetric experiments (Fig. 4). At a temperature of 180 °C and an O₂/MeOH ratio of 0.5, the catalyst weight increased over time levelling off at about 4.6%. This corresponds well to the theoretical value of 4.4% that is expected for the complete oxidation of Cu⁰ to Cu^I (Cu₂O). It can therefore be concluded that under these conditions not only the surface but also the bulk is oxidized and Cu₂O is the dominating phase. The Cu^I content of the catalyst at different temperatures was estimated by

the observed mass changes (Fig. 5). It can be seen that up to ca. 200 °C Cu^I is the dominating oxidation state. With increasing temperature the fraction of Cu^I decreased. At 250 °C the catalyst is totally reduced (Cu⁰).

The observed decrease of the oxidation state with increasing reaction temperature is also supported by XPS studies on the same catalyst at similar reaction conditions which revealed that Cu^I was the predominating surface oxidation state (ca. 90%) at low temperature (197 °C). At 257 °C a copper (I) content of ca. 20% was found [15]. The reported Cu^I contents of the XPS study are higher than the results of this study. This may indicate a concentration of Cu^I species at the surface of the catalyst since XPS is a surface-sensitive method.

A decrease of the oxidation state with increasing temperature is also reported for the oxidative methanol reforming over a binary CuO/ZnO catalyst which was investigated by in-situ time-resolved X-ray absorption near-edge spectroscopy (XANES) [21]. At 170 °C, a reoxidation of Cu⁰ to Cu^I was observed upon cooling the reactor from 240 °C under reaction conditions. The formation of Cu^{II} was ruled out.

Böttger et al. studied a model copper catalyst for the methanol partial oxidation. The active phase of the catalyst was found to be a copper suboxide phase (Cu_(x≈10)O) located at the surface and the near-surface region [17]. However, the presence of such a suboxide layer in the reduced operating catalyst could not be verified by the TGA measurements since the sensitivity of the measurement under the conditions applied was not sufficient to detect such small weight changes. No weight gain was observed at 250 °C compared to the reduced catalyst (Fig. 4, section F, 250 °C). It should be noted that also no weight increase over time was observed at lower oxygen-to-methanol ratios (sequences D and E), indicating that the copper remains in the reduced state (Cu⁰) under these conditions as well.

3.2.2.2. Methanol conversion. The methanol conversion was very low when no oxygen was present in the feed (Fig. 6, before

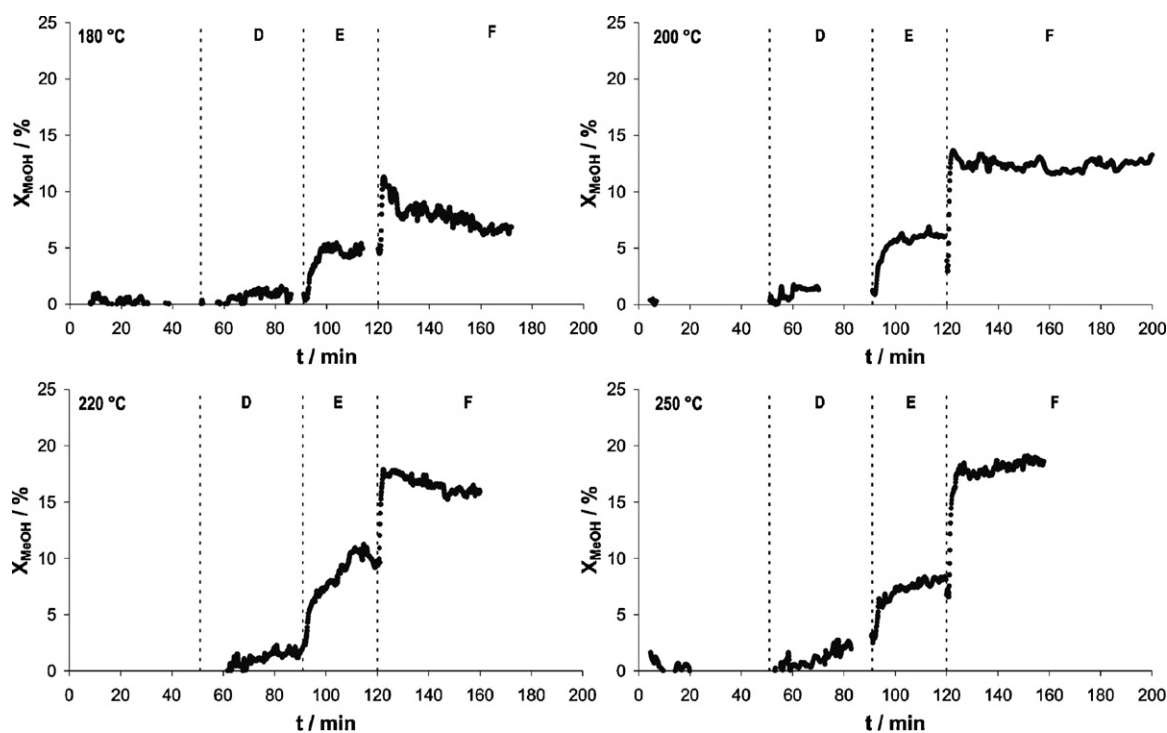


Fig. 6. Methanol conversion at several O₂/MeOH ratios and temperatures. (D) O₂/MeOH = 0.1, (E) O₂/MeOH = 0.2 and (F) O₂/MeOH = 0.5. Details of the sequences are presented in Table 1. The catalyst samples were prereduced.

sequence D). As expected, the conversion increased with increasing temperature and oxygen concentration in the feed. It should be noted that a maximum conversion of about 20% was observed in the TGA experiments which is lower than in the microreactor at 220 °C. This is partly due to the lower mean catalyst temperature in the isothermal TGA experiments and partly by incomplete contacting of the feed stream with the catalyst due to the geometry and flow pattern inside the TGA setup. On the other hand, if complete contacting of the gas with the catalyst is assumed, the WHSV would be a factor of ca. 4 higher than in the microreactor, which would also help in explaining the lower conversion in the TGA experiment.

3.2.2.3. Formation of methyl formate and formaldehyde. Oxygen-free decomposition of methanol. The evolved product gases were analysed by infrared spectroscopy (IR). The IR spectrum of the reaction products obtained after exposure of the reduced catalyst to methanol at 180 °C (sequence A) is displayed in Fig. 7 (spectrum b). The spectrum obtained after subtraction of the methanol reference (a) is also shown (d). The comparison of spectrum (d) with that of methyl formate (spectrum c) revealed that methyl formate is generated upon exposure of the reduced catalyst to methanol. Some carbon monoxide (absorption band at 2100 cm⁻¹ and 2200 cm⁻¹) as well as small amounts of carbon dioxide (2360 cm⁻¹) were also detected. Formaldehyde was not found in the effluent gas.

Several spectroscopic studies have been performed on the interaction of methanol with copper surfaces [33–39]. Methanol is dissociatively adsorbed forming methoxide species (–OCH₃), which can further react to formaldehyde species. If an excess of methanol was applied, methyl formate was found which can further decompose to give carbon monoxide (compare Eqs. (6) and (7)). Thus, the results of this study are in-line with the results in the

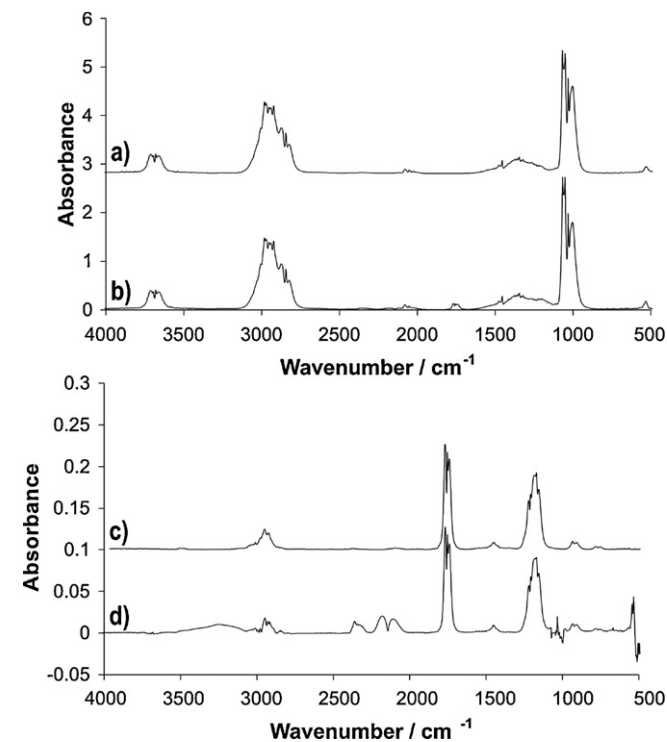


Fig. 7. Gas phase infrared spectra: (a) methanol, (b) spectrum of the reaction products obtained after catalyst exposure to methanol at 180 °C. No oxygen was present in the feed (sequence A in Fig. 3). (c) IR spectrum of methyl formate, C₂H₄O₂ (data taken from the NIST chemistry web book [32]) and (d) difference spectrum (b–a).

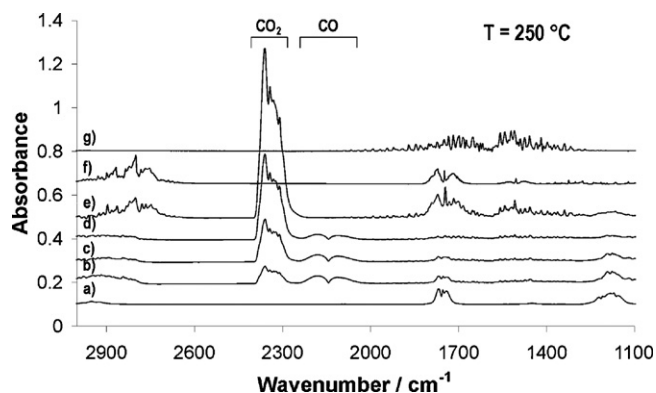


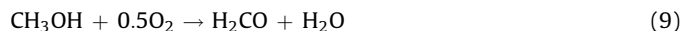
Fig. 8. Infrared spectra recorded at 250 °C at different reaction conditions. The methanol background was subtracted (a) methyl formate (reference), (b) MeOH/He, (c) O₂/MeOH = 0.1, (d) O₂/MeOH = 0.2, (e) O₂/MeOH = 0.5, (f) formaldehyde (reference, NIST chemistry web book [31]) and (g) water (reference, NIST chemistry web book [32]). The catalyst samples were prerduced.

literature obtained by other methods. The traces of CO₂ which are found in the spectra may be due to the decomposition of surface formate species.

Influence of the O₂/MeOH ratio. Fig. 8 shows the gas phase infrared spectra recorded at 250 °C at different O₂/MeOH ratios (Fig. 8, b–e) after the reaction was equilibrated as indicated by the TGA profiles (Fig. 4) and by the product evolution profiles (Fig. 10). The methanol background was subtracted. For comparison, reference spectra of methyl formate (HCOOCH₃, a), formaldehyde (H₂CO, f) and water (g) were included. Methyl formate was mainly formed after the introduction of methanol. With increasing oxygen concentration in the feed (Fig. 8, c and d) the intensity of the bands representative of methyl formate (1100–1250 cm⁻¹ and 1700–1800 cm⁻¹) decreased indicating a decrease of the amount of methyl formate produced. A different spectrum was obtained upon further increasing the oxygen concentration to an O₂/MeOH ratio of 0.5 (spectrum e).

The comparison with the reference spectra (f and g) revealed that formaldehyde is produced instead of methyl formate. Water was also produced and CO disappeared. The same trend was also observed at lower reaction temperatures (180 °C, 200 °C, 220 °C, not shown) after equilibration of the catalyst.

Obviously, the formation of methyl formate and formaldehyde depends strongly on the oxygen-to-methanol ratio. Methyl formate is formed mainly when no oxygen is present in the feed indicating that this reaction is favored over the fully reduced catalytic sites. If the oxygen content is increased, the amount of methyl formate decreases. Applying an O₂/MeOH ratio of 0.5 yields formaldehyde instead of methyl formate, indicating that the selective oxidation of methanol to formaldehyde (Eq. (9)) occurs under oxygen-rich conditions.



These results are in-line with the reaction mechanism proposed in the literature for various copper surfaces. Methoxy species formed on the surface are converted to formaldehyde which can either desorb or further react to CO₂ and hydrogen through the decomposition of surface formate species (compare Fig. 1).

The picture seems to be more complicated at lower temperatures (below 220 °C).

The TGA curves revealed that the catalyst is oxidized to copper (I) with increasing time-on-stream under oxygen-rich conditions depending on the reaction temperature (Fig. 4). Fig. 9 shows the corresponding absorbance data recorded at 1745 cm⁻¹

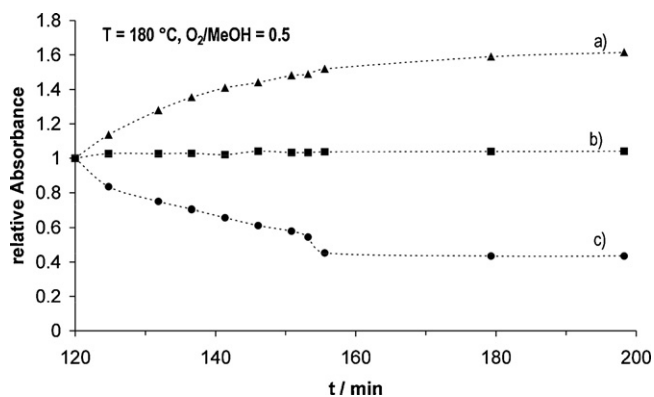


Fig. 9. Relative absorbance ($A_t/A_{t=120 \text{ min}}$) over time. (a) formaldehyde (1745 cm^{-1}), (b) MeOH (2981 cm^{-1}) and (c) CO₂ (2360 cm^{-1}) at 180 °C at oxygen-rich conditions (sequence F).

(formaldehyde, trace a), 2981 cm^{-1} (MeOH, trace b) and 2360 cm^{-1} (CO₂, trace c) over time for a reaction temperature of 180 °C. The data were normalized to the absorbance at a reaction time of 120 min. At this time, the oxygen content of the feed was increased to O₂/MeOH = 0.5. Clearly it can be seen that the relative absorbance at 1745 cm^{-1} increased over time whereas it decreased at 2360 cm^{-1} and remained more or less constant at 2981 cm^{-1} . Obviously, this oxidation influenced the selectivity of the catalyst: CO₂ selectivity decreased and formaldehyde selectivity increased when the catalyst was oxidized. The role of Cu^I species in the dry partial oxidation of methanol was discussed by Alejo et al. It was assumed that Cu^I species favored the formation of CO and water [14]. This suggestion is not confirmed by the present study which indicates that Cu^I enhances the formation of formaldehyde. In contrast to the experiment conducted at 250 °C where the catalyst remained in the reduced state, the oxygen in the feed penetrates the copper surface and forms copper (I) oxide. The increasing amount of copper (I) oxide could be an explanation for the increasing formaldehyde selectivity. Copper (I) oxide, Cu₂O, is a p-type oxide.

These types of oxides are known to form electron-rich adsorbed oxygen species (i.e. nucleophilic oxygen) which are more selective towards partial oxidation (i.e. formation of formaldehyde) and less selective to the total oxidation (i.e. formation of CO₂) [40].

From the results obtained it can be concluded that the optimal O₂/MeOH ratio (in terms of hydrogen yield) at 250 °C is about 0.2 since the yield of the hydrogen-containing by-products methyl formate and formaldehyde is reduced compared to higher or lower O₂/MeOH ratios. However, it has to be taken into account that carbon monoxide is formed at this condition which could be a problem for fuel cell applications.

3.2.2.4. Formation of carbon monoxide, carbon dioxide and water.

The evolution of carbon monoxide, carbon dioxide and water was directly monitored by IR absorption at the characteristic wave-numbers and is shown in Fig. 10. During methanol adsorption (sequence A), carbon dioxide and water are formed immediately after contacting the catalyst, indicating a further reduction of the catalyst. This is also supported by some of the TGA curves (Fig. 4) which revealed a decrease in weight (i.e. at 250 °C). Carbon monoxide was formed at oxygen-free or oxygen-lean conditions (sequence A and D, respectively) indicating that carbon monoxide is probably mainly formed by the decomposition of methyl formate (Eqs. (6) and (7)). The CO formation was strongly dependent on the reaction temperature. It was lowest at 180 °C

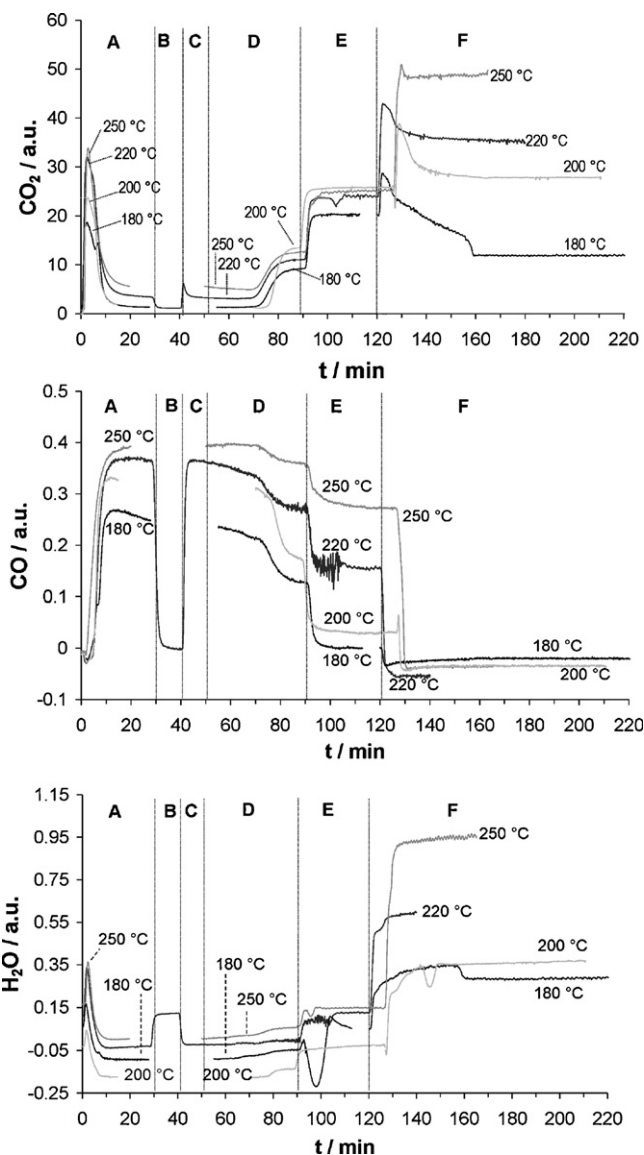


Fig. 10. Product gas evolution. A: He/MeOH, B: He, C: He/MeOH, D: O₂/MeOH = 0.1, E: O₂/MeOH = 0.2, F: O₂/MeOH = 0.5. Details of the sequences are presented in Table 1. The catalyst samples were prereduced. Interruptions are due to skipped sequences (B,C).

and highest at 250 °C. With increasing oxygen content (sequence E), the amount of carbon dioxide and water increased and the one of CO decreased. At oxygen-rich conditions (sequence F) CO could not be detected anymore. Thus, it can be concluded that carbon dioxide is not generated by the oxidation of carbon monoxide but from the decomposition of adsorbed formate species as proposed in the literature [24,25]. A strong influence of the reaction temperature on the product distribution was observed at oxygen-rich conditions (sequence F). At 250 °C, the evolution of CO₂ increased to a constant level after passing through a small maximum. At 220 °C and 200 °C, the CO₂ concentration showed a considerable decrease after passing the maximum value. At 180 °C, a strong decrease in CO₂ generation was observed which occurred in two steps (second step around 160 min). According to the previous discussion, we believe that the observed carbon dioxide profiles with increasing time-on-stream (section F) reflect the changes in the bulk oxidation state of the catalyst (i.e. formation of Cu^I).

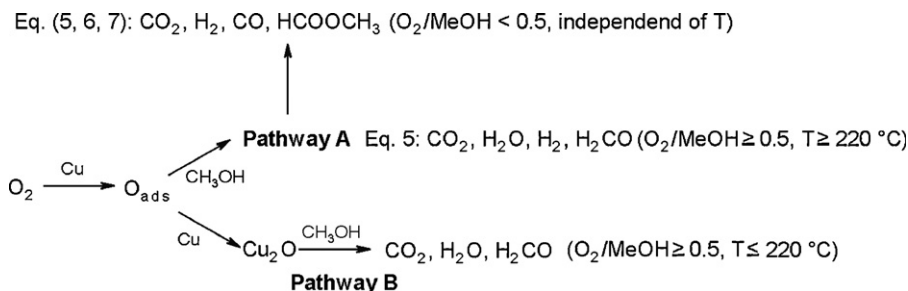


Fig. 11. Proposed reaction pathways of the oxidative decomposition of methanol on a copper catalyst.

4. Conclusions

The results of this study indicate that the reaction mechanism of the catalytic partial oxidation of methanol is strongly influenced by the oxidation state of the active copper phase which depends on the reaction conditions. We found that at least two different main pathways can occur (Fig. 11): oxygen is adsorbed on reduced copper sites and can react directly with adsorbed methanol species (pathway A). The copper remains in the reduced state. At low oxygen-to-methanol ratios (<0.5), methyl formate and carbon monoxide are formed as by-products independent of the reaction temperature.

At higher temperatures ($\geq 220^\circ\text{C}$) and higher oxygen-to-methanol ratios (≥ 0.5) formaldehyde is formed as a by-product instead of methyl formate. The catalyst remains in the reduced state.

A second reaction pathway (pathway B) can occur if the adsorbed oxygen oxidizes the active copper phase to cuprite (Cu_2O). The obtained results indicate also that pathway B reveals a higher selectivity to formaldehyde compared to pathway A. Reaction pathway B can only occur at low reaction temperatures (ca. $\leq 220^\circ\text{C}$) and high oxygen-to-methanol ratios (≥ 0.5) since otherwise adsorbed oxygen reacts faster with adsorbed methoxy species (or an intermediate species, e.g. HCHO) than with Cu resulting in a reduced catalyst.

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